The University of Chicago

THE HEATS OF DILUTION OF SULPHURIC ACID SOLUTIONS

A PART OF A DISSERTATION SUBMITTED TO
THE GRADUATE FACULTY IN CANDIDACY
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1931

By
WILLIS LAMBERT GROENIER

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INTRODUCTION

The recent interest in the nature of solutions has propagated a great variety of researches designed to test the validity of modern concepts and theories. Solutions of electrolytes cannot be thoroughly studied or understood until their activity coefficients are evaluated.

An accurate knowledge of the relative partial molal heat contents is essential to the complete evaluation of activity coefficients from freezing point determinations. For instance, Lewis and Randall[1] point out that if these heat terms are neglected the calculated activity of five molal sulphuric acid is in error by seventy per cent. The partial molal heat contents and their temperature coefficients can be evaluated from either heats of solution or heats of dilution data.

The apparent molal heat content of a solute in solution is defined as $\phi H = \frac{H_2 - n_1 H_1}{n_2}$, wherein H_2 is the heat content of the solution, $n_1 H_1$ the heat content of n_1 moles of the pure solvent, and n_2 the number of moles of solute.

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[1] Lewis and Randall. Thermodynamics. p. 354 McGraw-Hill. (1923).

From this relation it follows that heats of solution data equal a constant plus corresponding values of ϕ H, the apparent molal heat content. Absolute values of ϕ H have no significance. Relative values are sufficient for the calculation of relative partial molal heat contents. If values of ϕ H + C, derived from heats of solution data, are plotted against $\mu^{\frac{1}{2}}$ a curve is obtained that represents the integral heats of solution and may be called the "integral curve". See Fig. 1. μ represents the ionic strength.

The relative partial molal heat contents may be computed from the following relationships:

$$\bar{L}_1 = \frac{-m^{\frac{3}{2}} S}{2 \times 55.508}$$

and

$$\bar{L}_2 = (\phi H - \phi H^o) + \frac{m^{\frac{1}{2}}}{2} S$$

wherein S is the slope, $\frac{d(\phi H)}{d(\mu^{\frac{1}{2}})}$, of the integral curve and ϕ H the apparent molal heat content at $\mu^{\frac{1}{2}}$. The slope S cannot be evaluated with sufficient accuracy by any of the ordinary mechanical methods of differentiation.

The slope can be determined accurately by the method illustrated in Fig. 2. The average value of S between two values of $\mu^{\frac{1}{2}}$ is $\frac{\Delta(\phi H)}{\Delta(\mu^{\frac{1}{2}})}$. This represents the slope of a chord drawn between two points on the integral curve. $\frac{\Delta(\phi H)}{\Delta(\mu^{\frac{1}{2}})}$, the

average slope, may be calculated directly from either the difference between the measurements of two heats of solution or the measurement of a heat of dilution.

The data may be graphically represented by a plot of $\frac{\Delta(\phi H)}{\Delta(\mu^{\frac{1}{2}})}$ against $\mu^{\frac{1}{2}}$. Lines, or chords, are drawn, the ends of which correspond to pairs of values of $\mu^{\frac{1}{2}}$ and the ordinates of which are $\frac{\Delta(\phi H)}{\Delta(\mu^{\frac{1}{2}})}$. A smooth curve drawn through these lines may be called the slope or differential curve. It is obvious that by this method the ordinate of the slope curve at any value of $\mu^{\frac{1}{2}}$ represents the slope of the integral curve at that value of $\mu^{\frac{1}{2}}$.

This differential curve should be drawn through each chord of length $\Delta(u^{\frac{1}{2}})$ at such a point that the two areas between the two imaginary vertical lines at the ends of the chord, the chord itself, and the curve, are equal. While the experimental precision does not always permit this principle to be followed exactly, the best smooth curve may be drawn through the chords. In cases where the differential curve is essentially a straight line over the interval $\Delta(u^{\frac{1}{2}})$, it passes through the center of the chord. If $\Delta(u^{\frac{1}{2}})$ is long, however, and the curve is not a straight line, the chord will be intersected at a distance from the center depending on the amount of curvature. Vogel[2] discusses a method for the calculation

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[2]Young, T. F., and Vogel, O. G., J. Am. Chem. Soc., 54, 3030 (1932).

of the amount of this departure. This method may be used in conjunction with long chords to establish the position of the curve at various places, but there was no need to use it in this work.

In general, heats of solution data are very scant and those that do exist are unreliable. Brönsted[3] has determined the heats of solution of sulphuric acid at about 18° C. His measurements do not agree well with each other, particularly those for the dilute solutions. The recent work of Grau and Roth[4], also at 18° C., agrees well with that of Brönsted throughout the more concentrated solutions but again shows gross uncertainties in the dilute region.

Values of $\frac{\Delta(\phi H)}{\Delta(\mu^{\frac{1}{2}})}$ were calculated from Brönsted's measurements of the heats of solution and were plotted against $\mu^{\frac{1}{2}}$ in the manner already described. The differential curve obtained was indicative of a maximum slope value in the region of very dilute solutions. The data of Grau and Roth similarly treated did not indicate this behavior at all.

The work described in this dissertation was undertaken to study the course of the differential curve in the region of dilute and moderately concentrated sulphuric acid solutions. As described, heats of dilution data yield directly average

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[3]Brönsted, J. N., Z. f. Phy. Chem., 68, 693 (1910).

[4]Grau, R., and Roth, W. A., Z. f. Anorg. Chem., 187-189, 186 (1930).

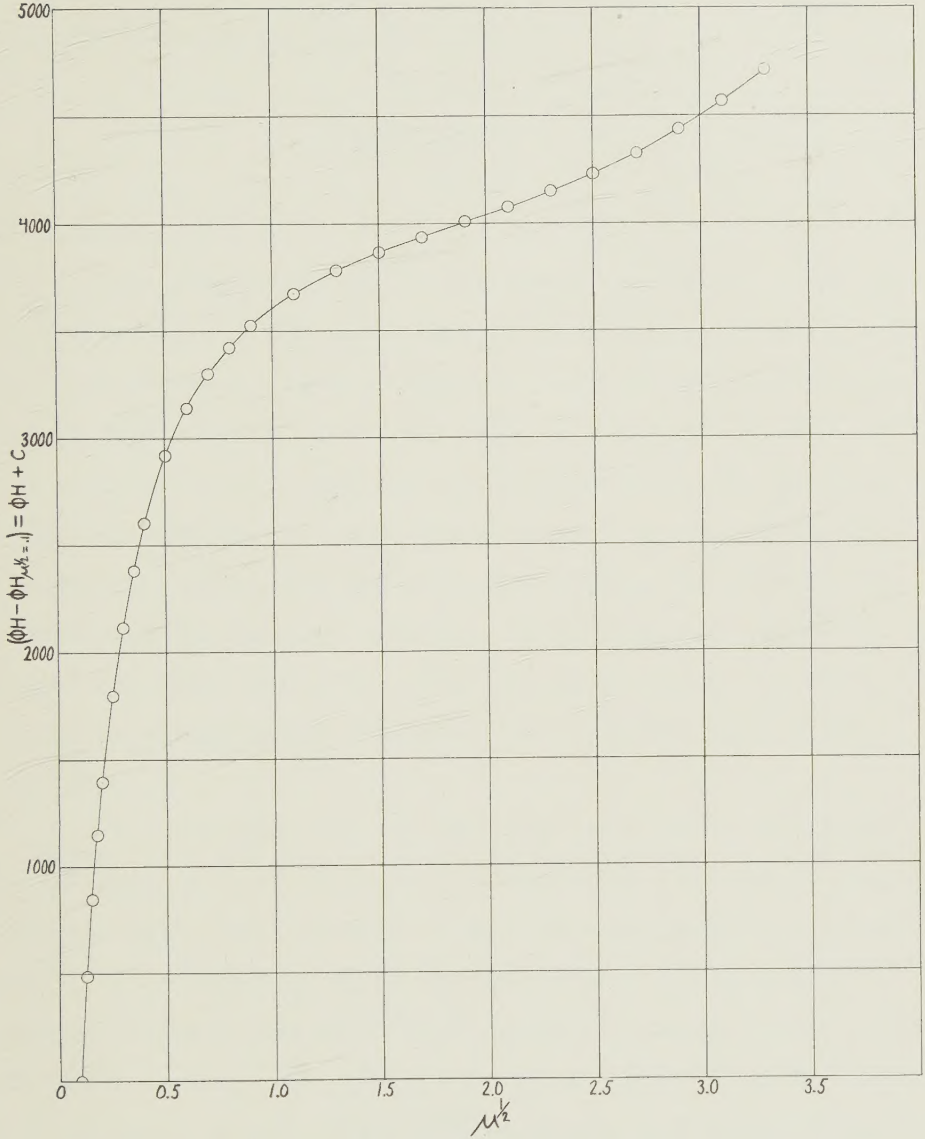
5000
4000
3000
2000
1000
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
$(\phi H - \phi H_{\mu^{\frac{1}{2}}=0}) = \phi H + C$
$\mu^{\frac{1}{2}}$

Fig. 1

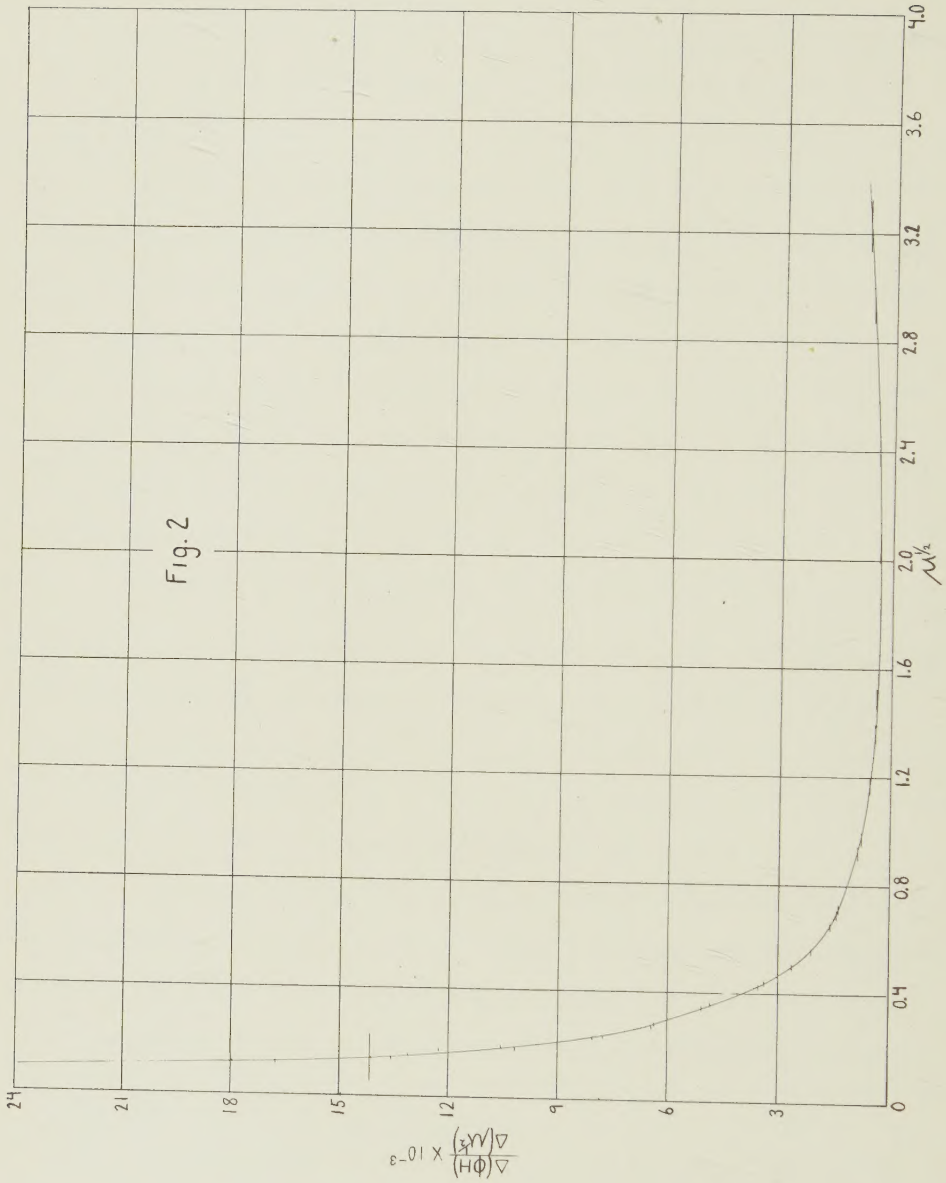
24
21
18
15
12
9
6
3
0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
4.0
$\nu^{1/2}$
$\frac{\Delta(\Phi H)}{\Delta(\lambda\lambda^2)} \times 10^{-3}$

Fig. 2

values of the slope, $\frac{\Delta(\phi_H)}{\Delta(\mu^{\frac{1}{2}})}$. With this end in view, heats of dilution measurements were undertaken.

THE APPARATUS

CALORIMETER.

The calorimeter was of the submerged-chamber type. See diagram by Vogel. It consisted of a wide mouthed silvered Dewar flask of about 1000 c.c. capacity cemented by means of litharge-glycerin cement to a brass ring to which the calorimeter top could be bolted. The top was provided with five chimneys to accommodate the auxiliary parts, namely, the container for the diluting water, the bulb-crushing device, the stirrer, the heater, and the thermel. The tops of the chimneys were provided with short pieces of rubber tubing so chosen as to fit the auxiliary parts and thus make the apparatus vapor-tight.

CONTAINER.

The container for the diluting water was a very thin-walled glass bulb of 75 to 85 c.c. capacity. The bulbs, made of pyrex glass, were blown in a bottle-shaped plaster-of-paris mould. A satisfactory way to crush the bulb was to rotate through 180° a closed metal tube fitted with three prongs. The metal used for the tube was tantalum, selected on the basis of resistance to acid, mechanical strength, and rather low heat conductivity.

However, the use of pyrex bulbs was not continued for long in this work. The reasons were chiefly two: (1) too frequently a piece of the broken glass would in one way or another interfere with the stirrer and thus produce enough heat to render the experiment valueless; (2) a correction term, determined by blank runs, of approximately .07 calories which resulted from the crushing of the bulb had to be applied to the data. Inasmuch as this .07 calories was only an average and not a constant quantity an error of .02 or .03 calories might be introduced. This is very important in the measurements on very dilute sulphuric acid solutions. Hence a metal mixing device that would have a constant "heat of opening" was sought. The one decided upon was made of pure silver.

The pure silver parts that composed the whole container were soldered together with silver solder, the composition of which was approximately two thirds silver and one third copper. A piece of the silver and one of the silver solder were weighed before and after twenty-four hours' contact with one molal sulphuric acid. The test showed that no reaction resulted. Each end of the container was provided with a cover of about one half the cross-sectional area of the can itself. The covers were sealed on with paraffin. A No. 26 platinum wire suspended from a metal rod inserted in one of the chimneys was connected to the top cover. Another platinum wire connected to the top cover was conducted around the bottom of the L-shaped pyrex rod that served to support the whole silver container, and was then

fastened to the bottom cover. The wires were attached to the ends of little tips that projected about seven millimeters over the ends of the covers. In this manner, both covers could be removed by withdrawing the wire less than one centimeter. A gentle pull of the wire was sufficient to break the paraffin seals. The ends of the silver container tapered down toward the covers and offered little resistance to the passage of liquid through the can.

STIRRING.

The stirrer for the calorimeter was made of a 1/8" rod provided with three four-blade propellers 1 1/8" in diameter. The metal used was tantalum. The stirrer was driven by a small synchronous motor geared directly to the stirrer. In this manner a very constant stirring rate was assured at all times, which is an indispensable feature of this method. The gears were of such ratio as to give the stirrer a speed of 450 R. P. M. That the stirring was adequate was confirmed by the absence of super-heating after a dilution and by the smallness of the lag.

THERMEL.

The thermel used in all the work was one of twenty-four junctions made of No. 26 constantan wire and No. 32 copper wire. Construction was according to the method of White[5]. The enclosing cases were of Pyrex glass. The constant temp-

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[5]White, W. P., J. Am. Chem. Soc., 36, 2292 (1914).

erature end was tightly fitted into a bulb-shaped silvered Dewar of about 250 c.c. capacity. Since this Dewar remained in the thermostat and was filled with the thermometer water, it afforded a very constant environment for the one end of the thermel. Thus any quick slight changes in the thermostat temperature were smoothed out. The thermel had a low resistance, about 46 ohms, and deflected the galvanometer about 13 mm. per microvolt. The thermel was calibrated approximately by comparison over fairly large temperature intervals[6]. The calibration did not have to be done accurately because it was used only to ascertain the absolute temperature inside the calorimeter.

THERMOSTAT.

The thermostat was equipped with an exceptionally long mercury regulator, the use of which kept the variations of temperature smaller than .001° C. Tests conducted with the free end of the thermel directly in the bath showed that temperature variations under ordinary working conditions were only .0001° or .0002° C. A Beckmann thermometer which had been compared with a Bureau of Standards thermometer was used to read the thermostat temperature. Inasmuch as the heat of stirring kept the calorimeter temperature somewhat above that of the thermostat, the latter was accordingly regulated to about 24.80° C. Thus the calorimeter temperature was in all experi-

[6]Calibrated by Vogel.

ments approximately 25° C.

POTENTIOMETER AND GALVONOMETER.

The wires connecting the calorimeter and standard resistances of the heater circuit to the potentiometer were suspended from the bottom sides of bakelite strips. The screws that supported the wires did not pass through the bakelite. In this way electrical leaks caused by accumulation of dust on top of the strips were precluded.

A White double potentiometer was used to measure the electromotive force of the thermel and the potential differences across the standard resistances of the heater circuit. The entire range of the instrument was 0.01 volts. An Eppley standard cell was used. A non-inductively wound copper coil of approximately the resistance of the thermel was connected to the potentiometer for the purpose of giving accurate readings of the galvanometer's neutral deflections. The working current was furnished by two large glass-jar storage batteries. They were mounted on a bakelite base and were separated by a sheet of bakelite. The whole unit was kept clean and dry. This arrangement and care were found to be indispensable in the prevention of electrical leaks. The batteries were connected to the potentiometer at all times and were very steady.

A Leeds and Northrup high sensitivity galvanometer was used in all the work. A neutral resistance of fine copper wire was shunted across the galvanometer to damp it critically. Although this reduced the sensitivity somewhat, the galvanome-

ter still gave a deflection of about thirteen centimeters per ten microvolts when the scale was about four meters away. The system was steady enough to read changes of the scale readings that corresponded to 0.01 microvolts. This corresponded to .00001° C. Room temperature fluctuations were diminished as much as possible, as they affected the galvanometer suspension. White's method of electrical shielding[7] was used throughout, and non-thermal connections were made in all cases[8].

TIMING MECHANISM.

Since in each experiment the heat capacity of the calorimeter and contents was determined by electrical heating, it was necessary to pass through the heater a very constant current. The batteries became constant after connection for fifteen minutes through an auxiliary resistance. It was equally important to time this current accurately.

The timing was accomplished by means of a seconds-pendulum clock with mercury contact, an automatic switch and two double-pole double-throw switches. Fig. 3 shows how these switches, the auxiliary coil, and the heater were incorporated into an electrical circuit. The automatic switch and the circuit were a revised form of the ones discussed by W. P. White[9]. The switch used in this work was made from a single-pole double-throw knife switch. The extended switch-knife was held on the upper contact, 1, by a catch which could be re-

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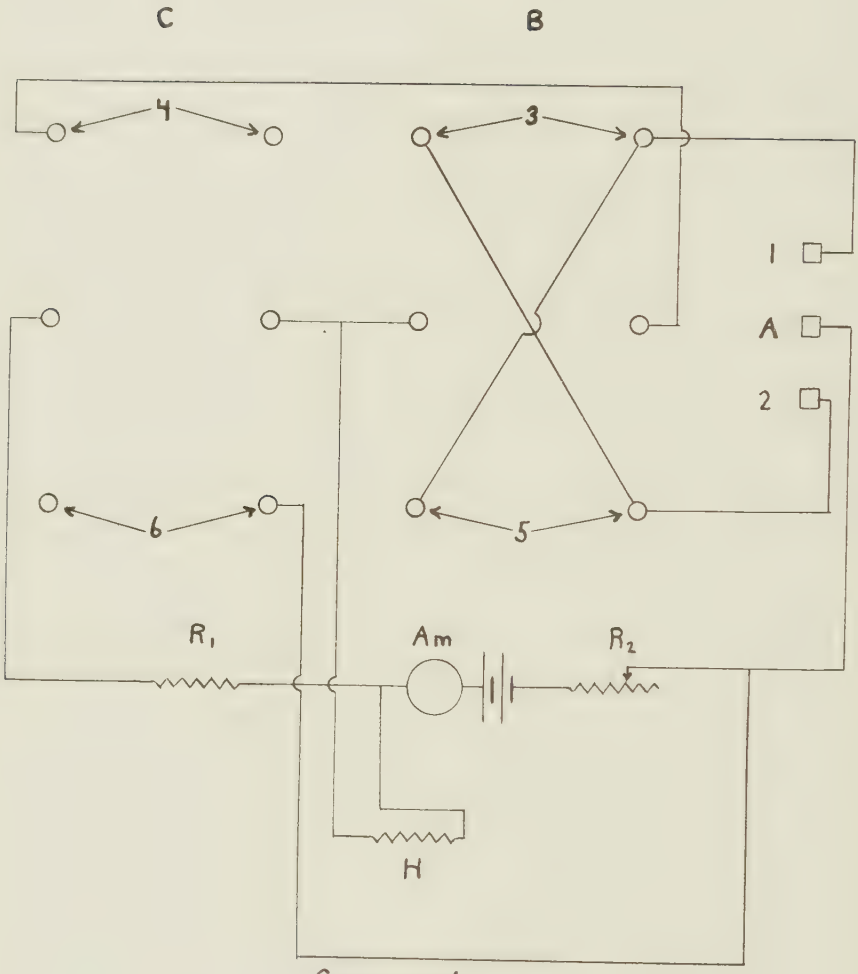
[7] White, W. P., J. Am. Chem. Soc., 36, 2011 (1914).
[8] White, W. P., J. Am. Chem. Soc., 38, 1856 (1916).
[9] White, W. P., Phy. Rev., 31, 688 (1910).

leased by an electromagnet. When free of the catch, the knife could descend to the lower contact, 2, under action of a spring.

At the beginning of a dilution experiment the automatic switch, A, was set on contact 1, and the double-pole double-throw switches, B and C, were set on contacts 3 and 4 respectively. See Fig. 3. The switches set at these positions allowed the battery current to flow through the auxiliary coil. On the desired second the circuit through the clock and electromagnet of switch A was closed. The excitation of the magnet released the catch and allowed the switch-knife to move from 1 to 2. By this action the battery circuit was closed through the heater.

The double-throw switches, C and B, set on the contacts 4 and 3, were then changed respectively to the contacts 6 and 5. Switch A was then raised to contact 1, and the double-pole switch was opened. All of these actions required no more than about five seconds, and none of them interrupted the flow of current through the heater.

The current then flowed for the remainder of the heating period through switches A and B connected in series. At the end of the heating period, which was usually 180 seconds in length, the catch of the automatic switch A was again excited by the electromagnet and caused to descend to contact 2. By this action the heater circuit was opened. It was in this manner that a heating period of any desired length was accur-



See next page.

Fig. 3

Key to Fig. 3

A . . . Automatic switch.

1 . . . Upper contact

2 . . . Lower contact

B . . . Double pole-double-throw switch.
Diagonally opposite contacts connected by wires that were conducted underneath the switch-base.

3 . . . Upper contacts

5 . . . Lower contacts

C . . . Double-pole double-throw switch.

4 . . . Upper contacts

6 . . . Lower contacts

R_1. . . Auxiliary resistance about equal to that of the heater.

R_2. . . Variable resistance.

Am. . . Ammeter.

H . . . Heater.

ately measured.

There was of course a time lag when the automatic switch moved from contact 1 to contact 2. Although this lag was in itself small, we had really two lags which very nearly canceled each other--one when the current was directed into the heater; and one when, by precisely the same action of the switch, it was cut off.

Another error that could have entered into such a circuit is considered in the following. The actual path of the heater current was slightly different at the time the current was measured on the potentiometer from what it was for a few seconds immediately after the automatic switch blade was dropped to contact 2. This meant a slightly different resistance in the heater circuit and hence a slightly different current value for the first few seconds of flow from that measured on the potentiometer. Possibility of this error was recognized and the circuit accordingly wired with heavy copper wire. That this error was negligible was shown by the fact that with the current flowing over either path no difference in current value could be detected on the White potentiometer. The clock was of the "weight" type and proved to vary not more than eight seconds per week. It is obvious that any error introduced by the clock was negligible.

The fact that the sum of all the errors in a heating period was of no importance was demonstrated by the experiments described on page 24.

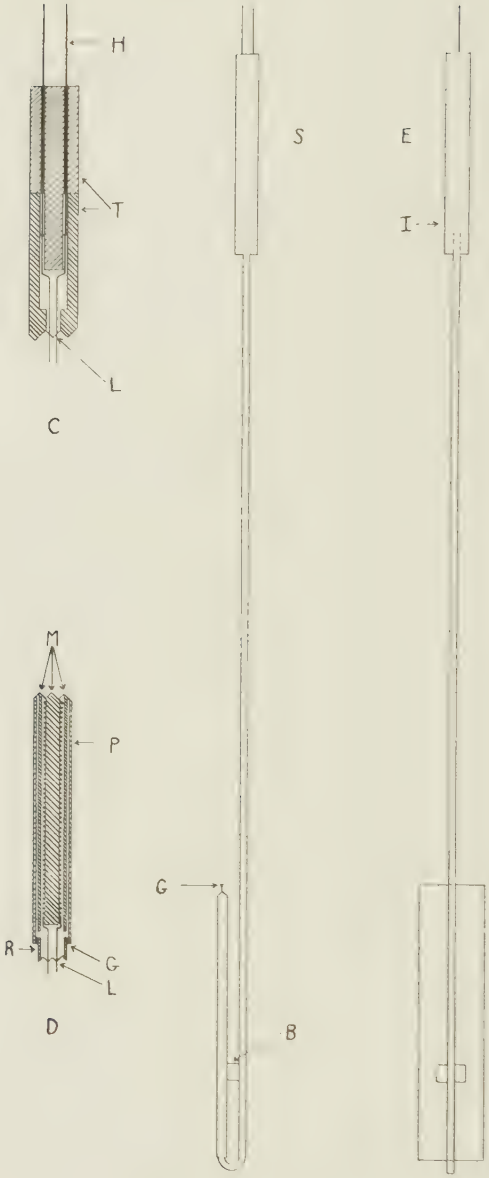
HEATER.

Two electrical heaters were made like the one shown in Fig. 4. The case was made of pure platinum, and the long thin tube encasing the lead wires was of platinum (95%) and iridium (5%). The latter was so chosen both for its additional mechanical strength and for its lower heat conductivity. Neither metal was at all attacked by the sulphuric acid solutions.

The heating element was a coil of No. 40 constantan wire wound about a heavy mica strip. Thin mica sheets cut a little larger than the size of the coil were placed on either side of the coil to insulate it from the case. No. 26 copper was chosen for the lead wires. The other ends of the lead wires were fastened to pieces of heavier copper wire which were held apart by a piece of bakelite rod that was made to fit over the platinum-iridium tube. The bakelite was fastened to the tube with litharge-glycerin cement, and this also served to close off the top of the heater.

The platinum-iridium tube encasing the lead wires was attached to the bottom of the heater rather than to the top because in the former position the tube had to pass through a longer column of liquid, which diminished the heat leak up the tube. All the metal joints of the heater were made tight by soldering with pure gold. See Fig. 4 for details of heater construction. The lag of such a heater is small.

Tests were made repeatedly throughout the work to see that there was no electrical leak between the coil and the



See next page.

Fig. 4

Key to Fig. 4

E.....Rear view of heater.

S.....Side view of heater.

I.....Litharge-glycerine cement used to fasten bakelite top to the platinum-iridium tube.

G.....Gold seals.

B.....Brace for platinum-iridium tube.

C.....Top section of bakelite top.

H.....Heavy copper wire leads.

T.....Bakelite.

L.....No. 26 copper wire leads.

D.....Section of lower part of platinum case.

P.....Platinum wall of case.

M.....Sheets of mica. Actually, the thin mica sheets are in contact with the platinum wall and with the heater coil.

R.....Platinum-iridium tube.

case. The test always used was a very severe one, as it employed the sensitive galvanometer set-up. As will be described later the heater was connected to the potentiometer-galvanometer circuit in such manner as to make possible a very accurate reading of the current flowing through the heater circuit. In these tests the regular source of current for the heater, about thirty-five volts, was applied across the coil and the platinum case. Under this potential the current that leaked across never deflected the galvanometer more than two millimeters.

The heater was of the high-resistance type (about 918 ohms) and hence carried a small current. The current was furnished by a fifty-volt battery with rheostat to adjust the current to an optimum value. The heater current was measured on the "P" side of the White double potentiometer during the heating period. Temperatures of the calorimeter were measured on the "Q" side. After the experiment was completed the resistance of the heater was measured by use of both "P" and "Q" sides of the potentiometer. The heater was connected as part of a shunt hook-up with three standard resistances as shown in Fig. 5.

The current in the heater during the heating period is given by $H_c = 0.1\ P$. The "P" and "Q" readings, taken after the experiment was over, gave the heater resistance from the following relationship: $H_r = \frac{Q}{P}(1000.1) - 0.1$. The resistances across which the potentials are read must be connected

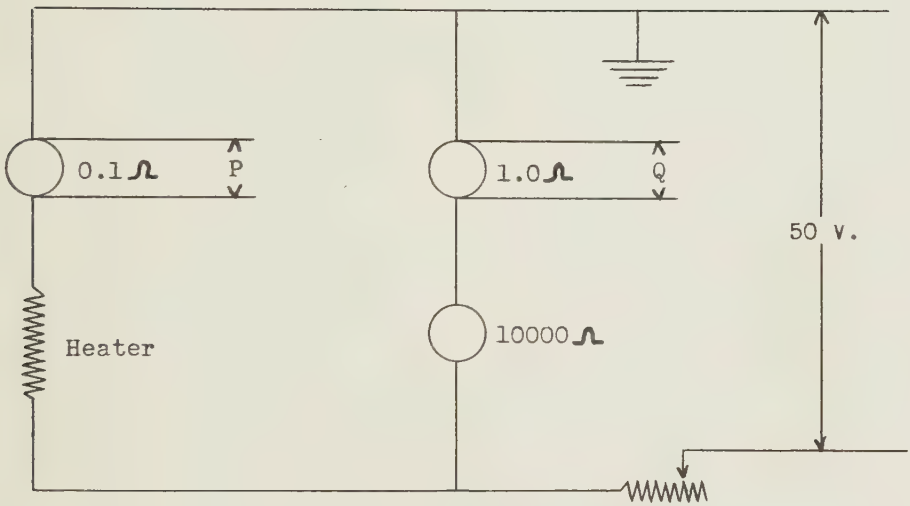


Fig. 5.

in the positions shown, that is, both on the grounded sides of the battery in order to prevent any leakage through the measuring instrument to the ground. The resistance of the heater was remarkably constant. Throughout the work the total variation was not over 0.02%.

STANDARD RESISTANCES.

The three standard resistances were mounted inside of a bakelite box. In this way they were well protected from moisture and dust. The shunt circuit involving these standard resistances and heater (see Fig. 5) was wired very carefully. Any places in the circuit that demanded a very low resistance wire were observed. No. 14 copper wire was used to connect the resistances and heater. All connections were made as short as possible. No. 18 copper wire was used for the leads to the "P" and "Q" sides of the potentiometer. The circuit thus wired permitted an accurate evaluation of the heater's resistance.

PREPARATION AND ANALYSIS OF THE SOLUTIONS

All of the sulphuric acid solutions were made up from stock solutions. These stock solutions were made from C. P. 100% sulphuric acid and were analyzed by the gravimetric $BaSO_4$ method. A few of the stock solutions also were analyzed by titration with standard NaOH. Benzoic acid was used as the primary standard. The two methods gave results that agreed

excellently. Distilled water was used for all the solutions whose molality was about 0.03 or more. For solutions more dilute than this, conductivity water was used; because in this region every precaution had to be taken against an error in the heat of dilution measurement. Conductivity water was used as the diluting water in all experiments. All dilutions were made by weight.

TESTS OF APPARATUS

In this type of calorimetry the initial temperature slope, that is, the temperature slope of the pre-experimental period, must be quite small. It was found that this initial slope must not be more than about .00003° C. per minute. If the temperature change is greater than this, the temperature of the calorimeter contents is slightly above or slightly below that of the container of diluting water. Obviously an experiment under such conditions would be useless.

Several blank experiments were performed with the calorimeter containing the silver container of diluting water to investigate what heat, if any, was liberated when the paraffin seals on the top and bottom covers of the can were severed. Obviously, to allow a suitable correction to be applied to the heat of dilution measurements, it is essential that any heat liberated by the action of opening the can be the same in each experiment. Distilled water was used in both the calorimeter

and the silver can. The blank experiments were conducted in precisely the same manner as any dilution experiment. The paraffin seals on the top and bottom covers of the container broke so easily when the platinum wire attached to them was pulled that no "heat of opening" was observed. This is a desirable feature of the apparatus, as it eliminates the necessity of a correction on the heat of dilution data.

The heat capacity of the calorimeter and contents was measured by the observation of the temperature rise following the introduction of a measured quantity of electrical energy.

The precision of the method employed was tested by means of the following experiments. The calorimeter, with parts as used in any dilution experiment, was filled with water. After a steady temperature state was attained, three heating periods of 180 seconds, 40 seconds, and 180 seconds, respectively, were conducted. The respective values in calories per microvolt were .8240, .8245, and .8244. It is seen that the greatest deviation from the mean is about 0.04%. Precision is very important for an accurate evaluation of the temperature change of any dilution.

The precision of which the apparatus as a whole unit was capable was examined also. This was done by measuring the heat of solution at 25° C. of solid sodium chloride. The finely ground salt was held in a small thin-walled pyrex-glass ball which broke very easily. A value of 1012 calories per mole of sodium chloride was obtained. The concentration of

the resulting solution was 1.054 g. sodium chloride per 100 g. of solution. The heat of reaction of the finely powdered salt was determined, from the temperature measurements, by the graphical method. This method was applicable because the reaction was of short duration. The value of the heat of solution per mole for this concentration, given by the careful measurements of Lipsett, Johnson and Maas,[10] is about 1013 calories. The two values are in practically perfect agreement.

The whole apparatus was given another test. Two dilution experiments were conducted on two samples of the same solution of sulphuric acid. $m_1 = 2.9370$. $\mu_1^{\frac{1}{2}} = 2.96833$. The quantity of acid and the quantity of diluting water were nearly the same in each experiment. The data were:

(1) $\mu_2^{\frac{1}{2}} = 2.87353$ $\qquad$ $S = 601.96$

(2) $\mu_2^{\frac{1}{2}} = 2.87614$ $\qquad$ $S = 602.06$

Since $\Delta\mu^{\frac{1}{2}}$ was not exactly the same in both experiments, the value of S given by experiment (1) was corrected to correspond to the value of $\Delta\mu^{\frac{1}{2}}$ of experiment (2). The two values of S, 602.32 and 602.06, could then be compared directly. They differ by about .04%. This is good agreement.

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[10] Lipsett, Johnson and Maas, J. Am. Chem. Soc., 49, 1940 (1927).

THE EXPERIMENTAL PART

An experimental determination involved the measurement of the heat liberated when a weighed quantity of water was mixed with a weighed amount of solution of known molality. A difference in e. m. f. was produced by the thermel from the temperature rise, and its equivalence in calories was obtained by calibration of the system through the introduction of a measured quantity of electrical energy.

The preparation of the apparatus for an experiment was precisely the same as that discussed by Vogel, with the one difference that the container for the diluting water was a silver one instead of a glass bulb. The experiment itself was also conducted after the manner described by Vogel. The calibration of the system, however, was conducted in a manner that was a little different. The heater current was turned on and, after the three-minute heating period, turned off by means of the clock and automatic switch mechanism already described. By this means the heater current was timed much more accurately than it could have been done with a stop-watch. On each experiment two heater runs were made, and the two values obtained in calories per microvolt never differed by more than 0.1%.

A typical experiment will be discussed with reference to the time-e. m. f. curve (Fig. 6) to illustrate the method of calculation of the data. The galvanometer deflections were

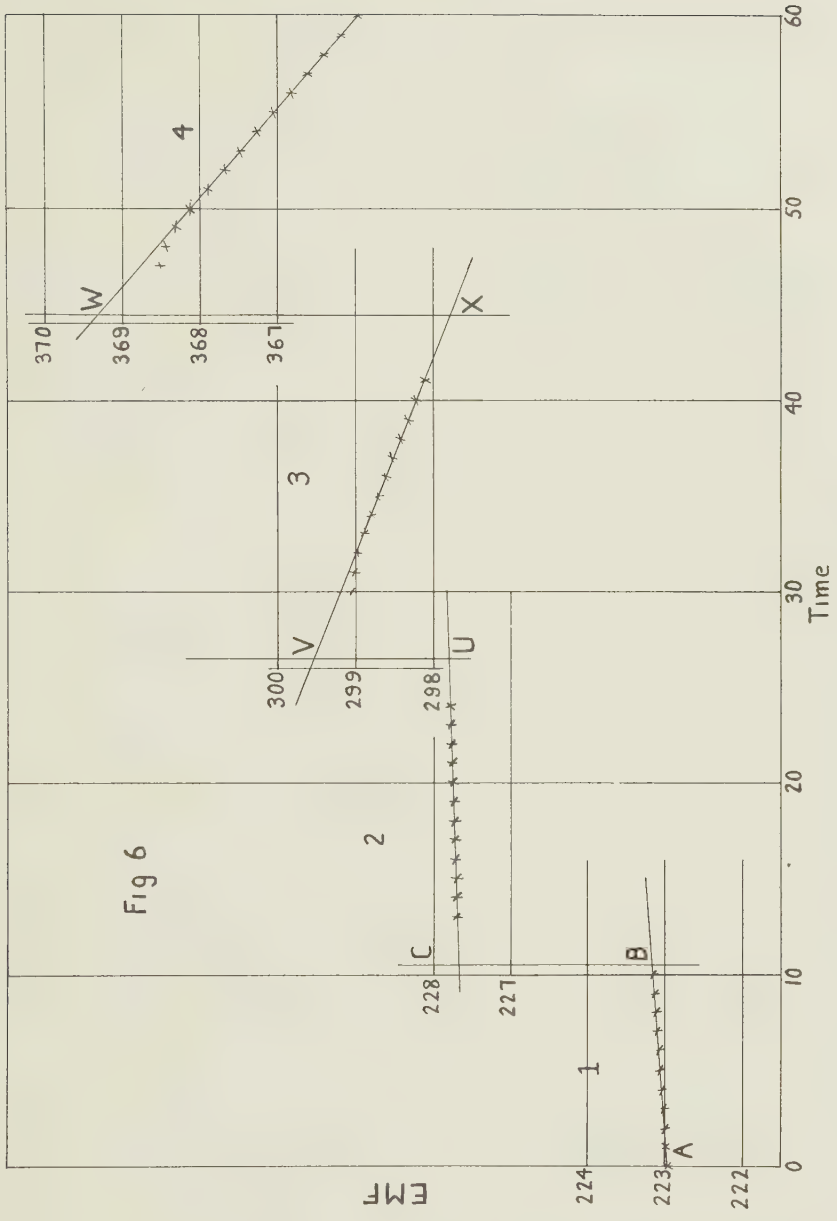
EMF
Time
0
10
20
30
40
50
60
222
223
224
227
228
299
300
367
368
369
370
A
B
C
U
V
W
X
1
2
3
4

Fig 6

first converted to e. m. f. values in microvolts and each value added to the corresponding potentiometer reading. The e. m. f. values were then plotted against the time in minutes. From this graph the actual heat changes of both the reaction and the heater runs were measured. The heat of reaction was assumed to be instantaneous, and accordingly the rise was measured by reading the intercepts of the vertical line B. C. The line B. C. corresponds to the time at which the solution and water were mixed. The temperature rise during each heater run was determined similarly from the intercepts on the vertical lines U. V. and X. W., respectively. The way in which these lines were located is described by Vogel. It is to be noted that each of the four sections of the experiment is plotted on a separate large scale of ordinate. This was done to improve the precision of reading the various intercepts. The four sections of the experiment may be called: (1) pre-experimental period, (2) post-experimental period, (3) and (4) post-heating periods.

Quite often calorimetric temperature changes of this type are calculated by means of the Regnault-Pfaundler method discussed by White.[11] This method makes use of an equation which corrects the change in temperature observed during the experimental period. However, the mathematical method is an improvement over the graphical only in cases in which the ex-

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[11] White, W. P., The Modern Calorimeter, Chem. Catalog Co., New York (1928).

perimental period is quite long, that is, in cases in which several minutes elapse before a steady temperature slope is again attained. That the graphical method was justifiable here was proved by calculation of some of the data by both methods.

The data of the particular experiment under consideration are given below. The electrical energy in calories of each heating period is given by $E = \frac{I^2Rt}{4.185}$. R, the resistance of the heater, as already shown is given by,

$$R = \frac{Q}{P}(1000.1) - 0.1 = \frac{.00363840}{.00396296} \times (1000.1) - .1 = 918.09 \text{ ohms.}$$

	Heater run 1	Heater run 2
e. m. f. (from curve)	71.73 microvolts	71.55 microvolts
Time	180 seconds	180 seconds
I	.0396910 amperes	.0396593 amperes
Energy = $\frac{I^2Rt}{4.185}$	62.21 calories	62.11 calories
Calories per microvolt	.8673	.8681
Average calories per microvolt		.8677

Heat of reaction (from curve) = 4.49 microvolts.

$\Delta H_{reaction} = 4.49 \times .8677 = 3.896$ calories.

The reaction that furnished this energy change was:

704.86 g. H_2SO_4 Sol'n (.08456 m.) + 75.32 g. H_2O = 780.18 g. H_2SO_4 Sol'n (.07633 m.).

Expressing this in another way:

5.7976 g. H_2SO_4 (in .08456 m.) + 75.32 g. H_2O = 5.7976 g. H_2SO_4 (in .07633 m.).

For the heat of dilution per mole we find:

1 H_2SO_4 (in .08456 m.) + X g. H_2O = 1 H_2SO_4 (in .07633 m.)

$$\Delta(\phi H)_{H_2SO_4} = 65.910.$$

Since here we want to compare $\frac{\Delta(\phi H)}{\Delta(\mu^{\frac{1}{2}})}$ to $\mu^{\frac{1}{2}}$ rather than to $m^{\frac{1}{2}}$ we must convert the molality to the ionic strength.

$\mu = 3m$. Hence $\frac{\Delta(\phi H)}{\Delta(\mu^{\frac{1}{2}})} = 2623.8$

RESULTS AND THEIR TREATMENT

The experimental results are shown in TABLE I. $\mu_1^{\frac{1}{2}}$ and $\mu_2^{\frac{1}{2}}$ are the square roots of the initial and final ionic strengths. $\Delta(\phi H)_t$ is the heat of dilution per mole at the temperature t. $\frac{\Delta(\phi H)}{\Delta(\mu^{\frac{1}{2}})}$ is the average slope over the interval.

Inasmuch as the temperature t at which the heat of dilution was measured is not exactly 25° C. a small correction is necessary. This correction can be made since $\frac{d\Delta(\phi H)}{dt} = \Delta(\phi C_p)$, wherein ϕC_p is the apparent molal heat capacity. Hence if ϕC_p is assumed constant over the very small temper-

TABLE I

$\mu_1^{\frac{1}{2}}$	$\mu_2^{\frac{1}{2}}$	$\Delta \phi H_t$	t	$\frac{\Delta(\phi H)}{\Delta(\mu^{\frac{1}{2}})}$
0.095687	0.091077	104.30	24.920	22624*
0.12302	0.11702	100.55	25.043	16758
0.12343	0.11732	109.75	25.064	17962
0.14165	0.13470	94.163	25.025	13548
0.14230	0.13516	100.77	25.041	14114
0.15622	0.14856	100.38	25.021	13104
0.17548	0.16670	107.47	25.027	12240
0.18207	0.17390	83.061	24.968	10166*
0.19628	0.18595	108.93	25.039	10544
0.22123	0.21220	72.859	25.006	8033.0*
0.22847	0.04442	2477.4	24.871	13457
0.22847	0.04576	2587.3	24.879	14162
0.22847	0.06885	2275.9	24.869	14259*
0.23056	0.21916	91.376	25.211	8015.4
0.23622	0.22539	83.929	24.991	7749.7*
0.27590	0.26262	85.431	25.033	6433.1*
0.28608	0.26987	102.99	24.966	6353.5*
0.28831	0.27403	91.176	25.053	6384.9
0.29428	0.27946	88.258	24.923	5955.3*
0.34301	0.32629	85.441	25.088	5110.1
0.35213	0.33468	88.480	25.001	5070.5*
0.36285	0.34502	86.453	25.194	4848.7
0.37676	0.35792	82.808	25.030	4395.3
0.43433	0.41352	73.253	24.979	3520.1*
0.44692	0.42473	75.001	24.969	3379.9*
0.50365	0.47853	65.910	25.050	2623.8
0.51059	0.48775	59.950	24.988	2624.8*
0.57004	0.54255	57.975	25.017	2108.9
0.66340	0.63422	46.451	24.978	1591.9*
0.71014	0.67838	45.007	25.002	1417.1*
0.73037	0.69394	50.228	25.041	1378.6
0.94345	0.89554	40.770	25.074	850.98
0.99709	0.94858	37.150	25.012	765.82*
1.19762	1.14039	31.531	24.948	550.95*
1.39484	1.32388	30.616	25.291	431.45
1.52996	1.44910	31.622	25.086	391.07
1.58394	1.50179	30.546	25.061	371.83
1.60275	1.52072	29.918	25.067	364.72
1.87238	1.77401	32.891	25.104	334.36
2.09700	1.98892	37.279	25.080	344.92
2.42497	2.35173	29.296	24.983	400.04
2.89315	2.86437	16.927	25.127	588.16
2.96833	2.87353	57.067	25.010	601.96
2.96833	2.87614	55.504	25.009	602.06
3.32233	3.13353	140.95	25.116	746.54

*Glass bulb employed. Silver container used in all others.

ature interval the correction is easily computed. Unfortunately, however, the specific heat data on sulphuric acid solutions are not sufficiently precise to yield concordant values of the apparent molal heat capacities. The specific heat data of Biron[12] are the most extensive and hence were used in the following calculations. Values of ϕC_p were calculated and plotted against $\mu^{\frac{1}{2}}$. The curve obtained had a small slope for all values of $\mu^{\frac{1}{2}}$ greater than 1.0. For values of $\mu^{\frac{1}{2}}$ less than 1.0 the course of the curve was not well defined, but it had a greater slope than that corresponding to the larger values of $\mu^{\frac{1}{2}}$.

In any case where $\mu^{\frac{1}{2}}$ is more than 1.0, the slope of the ϕC_p curve is small and hence $\Delta(\phi C_p)$ is small. This means the correction on $\Delta(\phi H)$ is small. An example will illustrate. Refer to TABLE I.

$$\mu_1^{\frac{1}{2}} = 1.19762 \qquad \phi C_{p_1} = 13.45$$

$$\mu_2^{\frac{1}{2}} = 1.14039 \qquad \phi C_{p_2} = 13.10$$

$$\Delta(\phi C_p) = .35$$

$$t = 24.948 \qquad \text{Hence } \Delta t = .052^{\circ}.$$

$$\Delta t \times \Delta(\phi C_p) = .052 \times .35 = .02 \text{ calories.}$$

$$\Delta(\phi H) = 31.531 + .02 = 31.551 \text{ calories.}$$

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[12] Biron. Quoted by Domke and Bein. Z. Anorg. Chem., 43, 148 (1904-5).

The value of $\frac{\Delta(\phi H)}{\Delta(\mu^{\frac{1}{3}})}$ then becomes 551.32 as compared to 550.95 when uncorrected. This small difference in the slope value does not exceed experimental error.

For values of $\mu^{\frac{1}{3}}$ less than 1.0 the ϕC_p curve has more slope but there, the chords of length $\Delta(\mu^{\frac{1}{3}})$ become shorter and hence $\Delta(\phi C_p)$ is small again. To illustrate again by example:

$\mu_1^{\frac{1}{3}} = .66340$ $\qquad$ $\phi C_{p_1} = 15.10$

$\mu_2^{\frac{1}{3}} = .63422$ $\qquad$ $\phi C_{p_2} = 15.35$

$\Delta(\phi C_p) = .25$

$t = 24.978$ $\qquad$ Hence $\Delta t = .022^{\circ}$

$\Delta t \times \Delta\phi C_p = .022 \times .25 = .006$

$\Delta(\phi H) = 46.451 + .006 = 46.457$

The value of $\frac{\Delta(\phi H)}{\Delta(\mu^{\frac{1}{3}})}$ then becomes 1592.1 as compared to 1591.9 when uncorrected. This difference is negligible.

As shown, the correction of $\Delta(\phi H)$ to 25° C. is very small if not negligible. However, these corrections would have been applied had the specific heat data been considered sufficiently reliable.

The values of S, that is, $\frac{\Delta(\phi H)}{\Delta(\mu^{\frac{1}{2}})}$, plotted against $\mu^{\frac{1}{2}}$, shown in Fig. 2 correspond to a quite smooth curve throughout the range studied. In the range from $\mu^{\frac{1}{2}} = 0$ to about 0.18 the curve is very steep and hence an accurate placement is very difficult. For this reason measurements were not attempted for values of $\mu^{\frac{1}{2}}$ less than 0.10. Between $\mu^{\frac{1}{2}} = 0.18$ and 0.10 an error of 0.1% in the molality produced an error in the slope of about 2%. This was the limit of accuracy in this region. Furtunately, in this very dilute region even crude data are sufficient for calculations of activity coefficients.

The slope curve could be well drawn throughout the whole region studied and extrapolated to $\mu^{\frac{1}{2}} = 0.10$ within the experimental accuracy. A maximum value in the slope curve at about $\mu^{\frac{1}{2}} = 0.25$ indicated by the data of Brönsted is not borne out by this work. As mentioned, the work of Grau and Roth did not indicate a maximum either. Integration of the slope curve over various intervals of $\mu^{\frac{1}{2}}$ yields directly values of $\Delta(\phi H) + K$, wherein K represents the area under the curve from $\mu^{\frac{1}{2}} = 0$ to 0.1. m = .00333. On the integral curve K represents $\phi H_{(\mu^{\frac{1}{2}} = .1)}$. Slope values can be read directly from the S curve. The relative partial molal heat contents, $\bar{L}_1$ and $\bar{L}_2$, can then be calculated (see TABLE II) from the relations shown on page 2.' Calculated in this way,

$\bar{L}_1 = \bar{H}_1 - \bar{H}_{1(\mu^{\frac{1}{2}} = .1)}$ rather than $\bar{H}_1 - \bar{H}_{1(\mu^{\frac{1}{2}} = 0)}$, and

$\bar{L}_2 = \bar{H}_2 - \bar{H}_{2(\mu^{\frac{1}{2}} = .1)}$ rather than $\bar{H}_2 - \bar{H}_{2(\mu^{\frac{1}{2}} = 0)}$.

TABLE II

$\mu^{\frac{1}{2}}$	$\bar{L}_1$	$\bar{L}_2$
	All Negative	
.10	0	0
.15	.03683	753.2
.20	.08893	1274.
.25	.1526	1653.
.30	.2332	1967.
.35	.3214	2218.
.40	.3984	2403.
.50	.5207	2641.
.60	.6505	2805.
.70	.8028	2933.
.80	.9620	3034.
.90	1.087	3106.
1.0	1.227	3166.
1.1	1.373	3216.
1.2	1.555	3263.
1.3	1.736	3303.
1.4	1.954	3342.
1.5	2.210	3379.
1.6	2.503	3415.
1.7	2.878	3453.
1.8	3.343	3492.
1.9	3.927	3535.
2.0	4.669	3581.
2.2	6.680	3687.
2.4	9.727	3815.
2.6	14.49	3978.
2.8	21.12	4173.
3.0	30.01	4399.
3.2	41.71	4660.

CONCLUSIONS

The heat data employed by Lewis and Randall in the calculation of activity coefficients were so meagre and inaccurate that they permitted little more than a type calculation. The numerical values themselves were of little significance. These new data will contribute to a significant estimate of the true activity coefficients. Before the calculation can be made finally, the heat of dilution measurements must be extended into the region of even more dilute solutions. This is now being done in this laboratory.[13]

The temperature coefficients of $\bar{L}_1$ and $\bar{L}_2$ are necessary also for a complete solution of the problem. These data for several electrolytes are now being obtained in other laboratories.[14]

SUMMARY

The heats of dilution of sulphuric acid solutions at 25° C. have been measured over a range in concentration of about .003 m. to almost 4.0 m. The corresponding values of $\mu^{\frac{1}{2}}$ are about 0.1 and 3.5, respectively. These measurements gave directly average values of the slopes of the integral heat of

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[13] C. E. Ronneberg, University of Chicago.
[14] F. T. Gucker, Jr., Northwestern University, and A. A. Sunier, Rochester University.

solution. The data were sufficiently precise to be represented accurately by a smooth curve. The slope curve was extrapolated to $\mu^{\frac{1}{2}} = 0.1$. A maximum slope value at about $\mu^{\frac{1}{2}} = 0.25$ indicated by the measurements of Brönsted was not found in this work.

The slope curve was integrated between $\mu^{\frac{1}{2}} = 0.1$ and numerous values of $\mu^{\frac{1}{2}}$. From these integral values and from the slope values themselves the relative partial molal heat contents at 25° C. were calculated. These were referred, therefore, to $\mu^{\frac{1}{2}} = 0.1$ and not to infinite dilution.

For his assistance and advice throughout the work the writer expresses to Dr. T. F. Young a sincere appreciation.